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(72) Inventor ALVIN EUGENE KONOPIK

(54) POWDERED POLYAMIDE COMPOSITIONS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to finely divided polyamides and processes for the production thereof.

Finely divided polyamides, in particular those having a melt index of less than 2000, are commercially available. Because polyamides are extremely tough, they have been found difficult to grind into powders even using the best commercially available grinding equipment. Polyamides in finely divided form are therefore relatively expensive, compared with granulates of the same material, because they have to be ground at extremely slow grinding rates.

Previously, powdered polyamides have been produced by cooling the polymer to below its glass transition temperature in liquid nitrogen or by adding solid carbon dioxide and grinding by brittle fracture. Although these grinding techniques enable faster grinding rates to be achieved than are generally possible at higher temperatures, they introduce other factors which themselves are expensive.

In recent years there has been considerable interest in joining pieces of textile material

using polymeric adhesives. Useful polymers should be low temperature fusible and should have good adhesive and toughness properties. These adhesives may be applied in a variety of forms such as films, threads, woven and nonwoven fabrics, and powders. Low melting polyamides have been found to be excellent adhesives for this application. One disadvantage of low temperature fusible polyamides, however, is that they cannot be economically produced in the form of the finely divided powder which is required for application by the popular sprinkle finish technique.

Finely divided polyamides would also be of value in the production of nylon color concentrates if they could be produced economically. Nylon color concentrates have generally been prepared by milling a powdered polyamide on a rubber mill with suitable pigments. Milling of a granular polyamide with a powdered pigment generally requires a considerable time because of the difficulty in obtaining a homogeneous dispersion of the finely divided pigment throughout the nylon. The use of a powdered nylon would facilitate a better premixing of the finely divided nylon with the pigment and would reduce the milling time at the fluxing temperature. A reduction in the fluxing time would be advantageous since polyamides are usually slowly degraded by prolonged heating.

According to one feature of the present invention there is provided a polymer composition in powder form which comprises a polyamide and an alcoholized ethylene/vinyl

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ester copolymer, the said powdered polymer composition being prepared by grinding the polyamide in the presence of the alcoholysed ethylene/vinyl ester copolymer.

5 According to a further feature of the present invention there is provided a method of powdering a polyamide wherein the polyamide is ground in the presence of an alcoholysed ethylene/vinyl ester copolymer.

10 According to a yet further feature of the invention there is provided a color concentrate which comprises a polyamide composition according to the invention and at least one coloring agent.

15 The invention further provides extruded articles containing color concentrates according to the invention dispersed in a resin and a method of bonding textile fabrics using a finely divided composition according to the invention.

20 The present invention is based upon the discovery that polyamides, conveniently having melt indices in the range of 0.1 to 2000, can be powdered at an improved rate by grinding in the presence of alcoholysed ethylene/vinyl ester copolymers. Preferably the grinding is carried out in the presence of 1 to 100 percent by weight, based on the polyamide, of the alcoholysed ethylene/vinyl ester copolymer.

25 The later preferably contains 70 to 98 mole percent copolymerized ethylene and (before alcoholysis) 2 to 30 mole percent copolymerized vinyl ester. The resulting finely divided polymer composition comprises the polyamide and the alcoholysed ethylene/vinyl ester copolymer and can for example with advantage have an average particle size diameter of 20 to 1000 microns.

30 A particularly preferred composition is one in which the polyamide has a melt index of 0.1 to 100, contains repeat units derived by weight 0 to 45 percent from the condensation of hexamethylene diamine and adipic acid, 0 to 65 percent from the condensation of hexamethylene diamine and polymethylene diacid of 10 to 12 carbons, and 20 to 75 percent from 6-aminocaproic acid, and has a melting point of less than 170°C.; the vinyl ester is vinyl acetate; and the alcoholysed ethylene/vinyl acetate copolymer is present in the amount of 2 to 75 percent by weight, based on the polyamide.

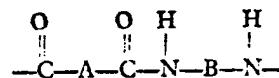
35 The grinding process of the present invention has been found to be particularly suitable for the grinding of polyamides having melt indices of less than 2000. These polyamides, commonly called nylons, include the polymers made by the intermolecular condensation of linear diamines containing 6 to 20 carbon atoms with linear dicarboxylic acids containing 2 to 48 carbon atoms. They also include polymers made by the intermolecular polymerization of omega-amino acids containing 4 to 18 carbon atoms.

40 These polyamides tend to be extremely

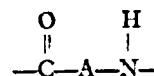
tough and consequently difficult to grind. Grinding in general is particularly difficult when the polyamide has a relatively low melting point. The process according to the invention may be used for polyamides having melting points for example of less than 200°C. and in particular when the melting point of the polyamide is less than 170°C.

45 The melting points described herein are measured by the well-known differential thermal analysis method, hereinafter referred to as DTA. In accordance with this method a crystalline sample is heated at a constant rate, for example, at 10°C. per minute, and the difference in sample temperature as compared with an inert non-crystalline sample in the same environment is recorded as a function of temperature. The peak temperature, that is, the temperature at which the differential temperature is maximum, is taken as the DTA melting point. Since polyamides having a low degree of crystallinity can be readily quenched to an amorphous state by rapidly cooling from above the melting point, the sample should be preconditioned so as to attain the crystalline state. Accordingly, the DTA melting point is determined using a dry specimen which has cooled from above its melting point at the rate of 1°C. per minute or slower.

50 A preferred class of polyamides for use in the process of this invention includes those containing repeat units derived by weight about 0 to 45 percent from the condensation of hexamethylene diamine and adipic acid, about 0 to 65 percent from the condensation of hexamethylene diamine and a polymethylene diacid of 10 to 12 carbons, and about 20 to 75 percent from 6-aminocaproic acid. These polyamides have melting points of less than 170°C. and thus are particularly useful as textile fusible adhesives. By "repeat units" is meant polymer units of the structure



and



in which A and B are the same or different polymethylene groups.

55 A particularly preferred class of polyamides includes those containing repeat units derived by weight 0 to 35 percent from the condensation of hexamethylene diamine and adipic acid, 5 to 50 percent from the condensation of hexamethylene diamine and polymethylene diacid of 10 to 12 carbons, and 25 to 65 percent from 6-aminocaproic acid. These preferred polyamides have melting points of less than 150°C.

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With regard to the above-described polyamides it is not necessary that the recited polyamide-forming monomers be used per se in the polymerization reaction. It is necessary only that the repeat units in the polyamide correspond to those derived from the recited monomers. The actual materials used in the polymerization reaction may be the recited monomers or polyamide-forming derivatives of these monomers, such as the acid chloride, ammonium salt, ester or half-ester. Suitable polymethylene diacids of 10 to 12 carbons include sebacic and dodecanedioic acids. Caprolactam may be used in place of 6-aminocaproic acid.

Suitable methods of preparing polyamides are well known to those skilled in the art. For example, the preparation of polyamides by melt condensation is described in U.S. Patent No. 2,252,555. The reaction is carried out by heating diacid, diamine and/or amino acid, or their polyamide-forming derivatives, at temperatures of 150° to 300°C. while driving off water, and continuing the reaction until the desired molecular weight is obtained. The functional groups at the end of the polymer chain will be carboxylic acid and amine, one of which may be in slight excess depending upon which reactant was present in excess.

The molecular weight of a polyamide is quantitatively related to its melt viscosity. Molecular weights are commonly indicated by the melt index which is an empirical measurement of inverse melt viscosity measured according to ASTM Test Method D-1238-65T. All melt index values used herein are obtained with the standard orifice at 190°C. using the 2160 gram weight, equivalent to 43.25 psi differential pressure. The melt index is the number of grams extruded in 10 minutes. The melt index of polyamides used herein should conveniently be at least 0.01 to provide processability and less than 2000 in order to provide adequate strength and toughness. Preferably, the melt index of the polyamide is 0.1 to 100.

The alcoholized ethylene/vinyl ester copolymers used as grinding aids in accordance with this invention are conveniently derived from copolymers which, before being alcoholized, contained 70 to 98 mole percent ethylene and 2 to 30 mole percent vinyl ester. Suitable vinyl esters for preparing these copolymers include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl palmitate and vinyl stearate. Vinyl acetate is the preferred vinyl ester for economic reasons. Preferably, the copolymer contains 75 to 95 mole percent ethylene and 5 to 25 mole percent vinyl acetate prior to being alcoholized.

Methods of preparing the ethylene/vinyl acetate copolymer precursors of the grinding aids used herein are well known to those skilled in the art as illustrated in U.S. Patent Nos. 2,200,429 and 2,703,794. Suitable

methods include high pressure polymerization and catalytic polymerization using free radical, ionic, and Ziegler type catalysts. According to commercial practice the resulting copolymer is pelletized by any of the known polymer cutting techniques such as strand cutting, melt cutting and dicing. Common pellet sizes correspond in volume to spheres having diameters of 1/6 to 1/4 inch.

The ethylene/vinyl ester copolymer should preferably be 50 to 100 percent alcoholized. By "50 to 100 percent alcoholized" it is meant that 50 to 100 percent of the acyl groups in the original copolymer are replaced by hydroxyl groups. These acyl groups may be alcoholized, that is, converted to hydroxyl groups, by any of the well-known methods including alcoholysis, hydrolysis or saponification. A suitable method of alcoholysis is described in British Patent No. 1,095,204. More preferably, the ethylene/vinyl ester copolymer is 75 to 100 percent alcoholized.

Improvement in the rate of grinding polyamides can be obtained with as little as 1 percent by weight, based on the polyamide, of alcoholized ethylene/vinyl ester copolymer. When more than 100 percent of alcoholized copolymer is present, no further significant improvement in grinding rate is achieved. Preferably, 2 to 75 percent by weight of copolymer, based on the polyamide, is present. Within this range substantial improvement in grinding rate is obtained. Most preferably, about 3 to 50 percent of copolymer, based on the polyamide, is present.

Any convenient equipment for grinding the polyamide may be used. Improvements in grinding rate of the order of about 2 to 3 times, or more than 3 times, have been achieved in accordance with this invention when using as little as 5 percent of the alcoholized copolymer grinding aid. Not only is the grinding rate improved in accordance with this invention, but in many types of grinding equipment, no sustained grinding rate can be obtained for many polyamides unless the grinding aid of this invention is present.

The method by which the grinding aid disclosed herein functions to improve the grinding rate of the polyamide is not fully understood. When using the grinding aid, the temperature of the product being discharged from the grinder can be allowed to rise without causing the product to agglomerate in the grinder. This in turn allows greater energy input to the grinder and increased grinding rates.

The finely divided compositions of this invention are useful in the preparation of color concentrates which are used in the coloration of nylon used to prepare fibers and molded plastic products. These color concentrates are prepared by milling the finely divided polymer composition of this invention with suitable organic dyes or organic or

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inorganic pigments. Suitable pigments include inorganic pigments such as rutile and anatase titanium dioxides, cadmium sulfides and sulfo-selenides, lead antimonate, nickel and chromium titanates, mercury cadmiums, chromates of nickel, tin and lead, ceramic greens such as chromium, cobalt, titanium and nickel oxides, ceramic blacks such as chromium cobalt an diron oxides, carbon black and ultramarine blue. Suitable organic pigments include phthalocyanine blues and greens and quinacridones. Suitable dyes include acid dyes such as sulpho rhodamine B and basic dyes such as the induline bases.

Polyamides melting below 170°C. and more particularly, below 150°C. are preferred for preparing color concentrates. These polyamides flux at a lower temperature thus providing a less severe thermal history for the polyamide and allowing the use of a wider variety of dispersing equipment. There is also less change of degrading the colorant when the dispersing is carried out at a relatively low temperature.

The amount of colorant contained in the colour concentrate may vary over wide limits. When it is important to minimize dilution of the nylon to which the color concentrate is added, a color concentrate having a maximum amount of colorant and a minimum amount of polyamide is desired. In this case the color concentrate could contain up to 80 percent by weight of pigment, based on the total color concentrate. The color concentrate is then let down into the desired nylon such as nylon 6, 66 or 610 to achieve the desired pigment level. When the colorant is a dye, the colorant content of the color concentrate may be as low as 0.1 percent since considerably less dye may be required in the final product, particularly when it is a tinted product. The preferred color concentrates are those containing 10 to 75 percent by weight of finely divided pigment, and most commonly, 15 to 30 percent pigment.

The color concentrate is commonly let down using conventional polymer extrusion equipment. The concentration of pigment in the final fiber or molded article is generally 0.01 to 1.0 part by weight of pigment per hundred parts of resin.

In addition to colorants, the color concentrate may also contain any of the other additives typically employed in polyamide technology including molding aids such as those described in U.S. Patent Nos. 2,948,698 and 3,009,900; nucleating agents such as those listed in U.S. Patent No. 3,080,345; heat stabilizers such as those described in U.S. Patent No. 2,705,227; antioxidants such as those listed in Modern Plastics Encyclopedia, Vol 45, No. 14A (McGraw-Hill Inc., Oct. 1968), Pages 505—507; antistatic agents such as those listed in Modern Plastics Encyclopedia, *ibid.*, Pages 500—501; flame retardants

such as those described in U.S. Patent Nos. 3,418,267; 3,440,211 and 3,468,843; fibrous, spherical and other forms of fillers and reinforcing agents, and mixtures thereof.

The finely divided compositions of this invention which contain relatively low melting polyamides are also useful as fusible textile adhesives which can be applied by the sprinkle finish technique. By this technique a coating of the finely divided polyamide composition is applied to the surface of a piece of textile material. At this stage the coating may be heated at a temperature above the melting point of the composition, if desired, to fuse the finely divided particles. The coating is then overlaid with a second piece of textile material and heat and sometimes pressure are applied, such as by ironing, thereby sealing together the two pieces of textile material. For this use the particles should have an average diameter of 200 to 1000 microns. Preferably, the particles have an average diameter of 100 to 800 microns.

The finely divided polyamide compositions of this invention are also suitable for other uses as will be apparent to those skilled in the art. For example, they are especially suitable for use in the fluidized bed coating of suitable objects. In this process the object to be coated is heated and then suspended in a fluidized bed of finely divided particles of this invention. The heat causes the polymer particles to adhere to the object and fuse together to form a coating.

The following examples are given without any intention that the invention be limited thereto. All parts and percentages are by weight.

Example 1

A polyamide was prepared as follows: To an autoclave was charged the following materials.

270	parts	hexamethylene	diammonium	
		adipate		
864	parts	hexamethylene	diammonium	110
		sebacate		
801	parts	ϵ -caprolactam		
5.9	parts	hexamethylene	diamine	
1.0	part	acetic acid		
1860	parts	water		115

The charge was heated under autogenous pressure to 250 psi; water was evaporated; and finally pressure was reduced to 26 inches of mercury vacuum while raising the temperature to 267°C. The polymer melt was extruded and chopped into about 1/8 inch granules. The polymer had a DTA melting point of 134°C. and a melt index of 2.8. Polymer ends were analyzed and found to be 40×10^{-6} eq./g. of carboxy-ends and 65×10^{-6} eq./g. of amine-ends. The above composition corresponds to 14.1 mole percent nylon 66, 37.3

mole percent nylon 610, 48.6 mole percent nylon 6, based upon two carboxamide groups per mole, that is, defining two caprolactam repeat units as one mole.

- 5 A copolymer of ethylene and vinyl acetate containing 82 mole percent ethylene and 18 mole percent vinyl acetate and being in the form of approximately 1/8 inch beads was alcoholized as follows: One hundred parts of
10 copolymer were suspended in 226 parts of methanol with 6.8 parts of sodium methoxide and heated from 50° to 64°C. over a period of 2 hours followed by heating at reflux for 3 hours. The resulting copolymer was 95
15 percent alcoholized.

- (A) Grinding of a 75/25 percent polyamide/copolymer mixture was carried out as follows: Six hundred pounds of the above polyamide and 200 pounds of the above
20 alcoholized ethylene/vinyl acetate copolymer were mixed and then fed to the feed hopper of a grinder which consists of 2 counter-rotating discs with variable tip clearances, both discs being milled and having close clearance
25 for the outer 3 inches of their diameters. The discs are about 30 inches in diameter and rotate at 3600 revolutions per minute in opposite directions giving a relative tip speed of about 56,000 feet per minute. Clearance
30 between the two discs decreases slightly across the milled section toward the outside, providing a smaller and smaller cross-section for a particle to escape through as it proceeds out between the two discs. The "V" grooves
35 milled in the disc are pitched about 5° in the reverse of the direction of rotation causing the material to be driven out more rapidly than discs with non-pitched grooves.

- The material was fed to the grinder
40 through the center of the disc so that all material passed outwardly through the clearance of the disc. The material was carried by air pulled into the grinder by the disc as air in-leakage. The air rate was 3,000 cubic
45 feet per minute at a temperature of between 13° and 15°C. A duct skin temperature limit of 60°C. was maintained on the duct approximately 2 feet above the exit of the grinder.

- The ground material was conveyed up
50 through a cyclone separator in which the particles were separated from the air stream and the particles were dropped on a 25 U.S. mesh size screen. The particles which did not pass through the screen were sent back to the
55 grinder as recycle. The ground material which passed through the 25 mesh screen was selected as product. The grinding rate was 360 pounds per hour.

- (B) The grinding procedure of (A) above
60 was repeated using a mixture of 1045 pounds of the above polyamide and 55 pounds of the above alcoholized ethylene/vinyl acetate copolymer. The grinding rate for this 95/5 percent polyamide/copolymer blend was 180
65 pounds per hour.

(C) For comparison, 1000 pounds of the above polyamide containing no alcoholized ethylene/vinyl acetate copolymer was charged to the grinder. Introduction of fresh feed was stopped when the duct temperature rose to 38°C. At this point recycle feed was continued and, when the duct temperature dropped to 35°C., fresh feed was automatically introduced into the grinder with the recycle feed. The sustained grinding rate was only 60 pounds per hour.

- (D) For further comparison, the procedure of (C) above was repeated except that the duct temperature was allowed to rise to 40.5°C. The polymer became tacky and matted together whereby no sustained grinding rate could be achieved.

Example 2

- (A) A colour concentrate containing 50 percent by weight pigment was prepared as follows: Seventy five grams of finely divided
85 Monastral Green B, GT-710-D pigment ('Monastral' is a Registered Trade Mark) and 75 grams of the finely divided polyamide/copolymer composition prepared in Example
90 1 (A) were placed in a quart can and thoroughly mixed by shaking for 5 minutes on a Red Devel shaker (a commercially available paint mixer). The resulting mixture was banded on a two-roll rubber mill operating
95 with the front roll at a temperature of 138°C. and at a speed of 10 rpm while the back roll was at 132°C. and a speed of 15 rpm. The nip opening between the rolls was 5 mils. Banding was continued for several minutes
100 until the material was well fluxed. The speed of the rolls was then changed so that the front roll was at 25 rpm and the back roll was at 15 rpm and the nip opening was adjusted to 25 mils. The milling was continued for an additional 10 minutes during
105 which time the stock was cut with a knife and returned to the mill to provide a homogeneous dispersion. The stock was then sheeted off and the sheet was broken into small pieces.

A small portion of the pieces of dispersion was placed between two plates, inserted into a press and reduced by heating and a pressure of about 50 tons to a thin film of about 5 mils thickness. The quality of the dispersion was examined by holding the film up to intense light and using a microscope having a magnification of about 45. These examinations indicated that a good dispersion of pigment had been obtained.

- (B) The above color concentrate containing 50 percent pigment was let down on a mill as follows: One hundred parts of the finely divided polyamide/copolymer composition prepared in Example 1 (A) were added to a two-roll rubber mill. A small amount of the above color concentrate (0.4 part) was added to the mill and banding was carried
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out as described above until a homogeneous dispersion was obtained. The final dispersion, which contained 0.2 part of pigment per 100 parts of resin, was examined as described above and found to be a good dispersion of pigment in polyamide.

(C) The color concentrate prepared in (A) above containing 50 percent pigment was let down (i.e. diluted with respect to the pigment concentration) in an extruder as follows: To a polyethylene bag was added 120 parts of small pieces of the color concentrate and 480 parts of the finely divided polyamide/copolymer composition prepared in Example 1 (A). The dry blend was shaken in the polyethylene bag until it was thoroughly mixed. The resulting mixture was added to a 1 inch Killion extruder (an extruder having a mixing screw of varying pitch), flighted torpedo screw; a spaghetti die (a die with a circular 0.125" diameter orifice), a single 30 mesh screen pack ahead of the die and cooling water on the hopper. The extrudate was passed through chilled take off rolls. The die temperature was set at 177°C. The barrel temperatures were 149°C. in the rear zone, 177°C. in the center zone and 182°C. in the front zone. The speed control dial was set at 4, the percent of maximum rpm was 18 and the indicated pressure was 700—750 psig. A good 10 percent dispersion was obtained. The spaghetti product was reduced in size by cutting with scissors.

(D) The above let down containing 10 percent pigment was further let down to 1 percent pigment as follows: To a polyethylene bag was added 100 parts of small particles of the 10 percent let down prepared above and 900 parts of the finely divided polyamide/copolymer composition prepared in Example 1 (A). The dry blend was thoroughly mixed and fed to the hopper of the extruder described in (C) above. The quality of the resulting dispersion was examined as described in (A) above. A good 1 percent dispersion was obtained.

WHAT WE CLAIM IS:—

1. A polymer composition in powder form which comprises a polyamide and an alcoholized ethylene/vinyl ester copolymer, the said powdered polymer composition being prepared by grinding the polyamide in the presence of the alcoholized ethylene/vinyl ester copolymer.

2. A composition as claimed in claim 1 wherein at least 1 percent by weight of the said copolymer based on the weight of polyamide is present.

3. A composition as claimed in claim 2 wherein at least 2 percent by weight of the said copolymer based on the weight of polyamide is present.

4. A composition as claimed in claim 3 wherein at least 3 percent by weight of the

said copolymer based on the weight of polyamide is present.

5. A composition as claimed in claim 4 wherein at least 5 percent by weight of the said copolymer based on the weight of polyamide is present.

6. A composition as claimed in any of the preceding claims wherein not more than 100 percent by weight of the said copolymer based on the weight of polyamide is present.

7. A composition as claimed in claim 6 wherein not more than 75 percent by weight of the said copolymer based on the weight of polyamide is present.

8. A composition as claimed in claim 7 wherein not more than 50 percent by weight of the said copolymer based on the weight of polyamide is present.

9. A composition as claimed in any of the preceding claims wherein the polyamide has a melt index of at least 0.01.

10. A composition as claimed in claim 9 wherein the polyamide has a melt index of at least 0.1.

11. A composition as claimed in claim 10 wherein the polyamide has a melt index of not more than 2000.

12. A composition as claimed in claim 11 wherein the polyamide has a melt index of not more than 100.

13. A composition as claimed in any of the preceding claims wherein the polyamide contains carbonamide groups linked by polymethylene groups.

14. A composition as claimed in claim 13 wherein the polyamide contains repeat units derived from 0 to 45 percent by weight of a condensation product of hexamethylene diamine with adipic acid, from 0 to 65 percent by weight of a condensation product of hexamethylene diamine with a polymethylene diacid containing from 10 to 12 carbon atoms and from 20 to 75 percent by weight of 6-aminocaproic acid.

15. A composition as claimed in claim 14 wherein the polyamide contains repeat units derived from 0 to 35 percent by weight of a condensation product of hexamethylene diamine with adipic acid, from 5 to 50 percent by weight of a condensation product of hexamethylene diamine with a polymethylene diacid containing from 10 to 12 carbon atoms and from 25 to 65 percent by weight of 6-aminocaproic acid.

16. A composition as claimed in any of the preceding claims wherein the polyamide has a melting point of less than 170°C.

17. A composition as claimed in claim 16 wherein the polyamide has a melting point of less than 150°C.

18. A composition as claimed in any of the preceding claims wherein the copolymer contains at least 70 mole percent of copolymerized ethylene.

19. A composition as claimed in claim 18

- wherein the copolymer contains at least 75 mole percent of copolymerized ethylene.
20. A composition as claimed in any of the preceding claims wherein the copolymer contains not more than 98 mole percent of copolymerized ethylene.
21. A composition as claimed in claim 20 wherein the copolymer contains not more than 95 mole percent of copolymerized ethylene.
22. A composition as claimed in any of the preceding claims wherein the alcoholized copolymer is derived from a copolymer containing at least 2 mole percent of a copolymerized vinyl ester before alcoholysis.
23. A composition as claimed in claim 22 wherein the alcoholized copolymer is derived from a copolymer containing at least 5 mole percent of a copolymerized vinyl ester before alcoholysis.
24. A composition as claimed in any of the preceding claims wherein the alcoholized copolymer is derived from a copolymer containing not more than 30 mole percent of a copolymerized vinyl ester before alcoholysis.
25. A composition as claimed in claim 24 where the alcoholized copolymer is derived from a copolymer containing not more than 25 mole percent of a copolymerized vinyl ester before alcoholysis.
26. A composition as claimed in any of the preceding claims wherein the alcoholized copolymer is derived from a copolymer containing copolymerized vinyl acetate before alcoholysis.
27. A composition as claimed in any of the preceding claims wherein the ethylene/vinyl ester copolymer is from 50 to 100 percent alcoholized.
28. A composition as claimed in claim 27 wherein the ethylene/vinyl ester copolymer is from 75 to 100 percent alcoholized.
29. A composition as claimed in any of the preceding claims wherein the powder has an average particle diameter of not less than 20 microns.
30. A composition as claimed in claim 29 wherein the powder has an average particle diameter not less than 100 microns.
31. A composition as claimed in any of the preceding claims wherein the powder has an average particle diameter of not more than 1000 microns.
32. A composition as claimed in claim 31 wherein the powder has an average particle diameter of not more than 800 microns.
33. A composition as claimed in claim 1 substantially as herein described.
34. A composition as claimed in claim 1 substantially as herein described in either of the Examples.
35. A method of preparing a composition as claimed in any of claims 1 to 34 wherein the polyamide is ground in the presence of an alcoholized ethylene/vinyl ester copolymer.
36. A method as claimed in claim 35 wherein the amount of copolymer present is as defined in any of claims 2 to 8.
37. A method as claimed in claim 35 or claim 6 wherein the polyamide is as defined in any of claims 9 to 17.
38. A method as claimed in any of claims 35 to 36 wherein the said copolymer is as defined in any of claims 18 to 28.
39. A method as claimed in any of claims 35 to 38 wherein grinding is effected to produce a powder having an average particle diameter as defined in any of claims 29 to 32.
40. A method as claimed in claim 35 substantially as herein described.
41. A method as claimed in claim 35 substantially as herein described in either of the Examples.
42. A polyamide when powdered by a method as claimed in any one of claims 35 to 42.
43. A color concentrate which comprises a polyamide composition as claimed in any of claims 1 to 34 and at least one coloring agent.
44. A concentrate as claimed in claim 43 which contains at least 0.1 percent by weight of coloring agent, based on the total weight of concentrate.
45. A concentrate as claimed in claim 44 which contains at least 10 percent by weight of coloring agent.
46. A concentrate as claimed in claim 45 which contains at least 15 percent by weight of coloring agent.
47. A concentrate as claimed in any of claims 43 to 46 which contains not more than 80 percent by weight of coloring agent.
48. A concentrate as claimed in claim 47 which contains not more than 75 percent by weight of coloring agent.
49. A concentrate as claimed in claim 48 which contains not more than 30 percent by weight of coloring agent.
50. A concentrate as claimed in any of claims 42 to 48 wherein the coloring agent comprises an organic dye or a pigment.
51. A concentrate as claimed in any of claims 43 to 50 which contains a molding aid, a nucleating agent, a heat stabilizer, an antioxidant, an antistatic agent, a flame retardant, filler or a reinforcing agent.
52. A color concentrate as claimed in claim 43 substantially as herein described.
53. A color concentrate as claimed in claim 43 substantially as herein described in Example 2.
54. An extruded article formed from a color concentrate as claimed in any of claims 43 to 53 dispersed in a resin.
55. An article as claimed in claim 54 which contains from 0.1 to 1.0 parts of pigment per hundred parts of resin.
56. A method of bonding textile materials which comprises introducing a composition as

claimed in any of claims 1 to 34 between
the surfaces to be bonded and heating whereby
the surfaces are bonded together.

57. Textile materials when bonded by a
5 method as claimed in claim 56.

For the Applicants,
FRANK B. DEHN & CO.,
Chartered Patent Agents,
Imperial House,
15/19, Kingsway,
London, W.C.2.

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